8.—THE ESSENTIAL OILS OF THE WESTERN AUSTRALIAN EUCALYPTS.

PART I.

THE OIL OF *E. FLOCKTONIAE*, MAIDEN,

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The monumental work of Baker and Smith on the eucalypts and their essential oils[1] deals mainly with the Eastern and Southern Australian species. Subsequent work in the Sydney Technological Museum by A. R. Penfold has been confined to the investigation of Eastern species and no attempt has been made to test the general conclusions advanced by Baker and Smith as far as the Western Australian species are concerned.

Baker and Smith examined some fifteen species from Western Australia; five of these (viz., *E. diversicolor, E. Lehmanni, E. cornuta, E. platypus* and *E. longicornis*) were trees cultivated in Melbourne; three (viz., *E. megacarpa, E. salmonophloia* and *E. accedens*) were of unknown origin, whilst the remaining seven (*E. calophylla, E. redunca, E. rudis, E. salubris, E. occidentalis, E. marginata* and *E. gomophocephala*) were from known localities in Western Australia.

The only other published work on Western Australian eucalypts appears to be that carried out by L. W. Phillips[2] on *E. spathulata* and *E. campaspe*.

These seventeen species comprise a very small proportion of the Western Australian eucalypts and it is obvious that before any attempt can be made to generalise, a systematic survey of the eucalypts must be made.

An examination of Baker and Smith's results shows that in Western Australia there occur the most primitive forms of the eucalypts, namely, *E. calophylla* (the red gum) and *E. diversicolor* (karri). The oils of these trees consist largely of pinene with only a very small amount of cineol present; the high boiling aldehydes (known collectively as aromadendral) and phellandrene are absent. The majority of the oils investigated by these authors, namely, those of *E. megacarpa, E. redunca, E. rudis, E. salmonophloia, E. accedens, E. Lehmanni, E. cornuta, E. platypus* and *E. longicornis*, are from more highly evolved species containing varying amounts of cineol, together with pinene, but not showing any evidence of the presence of phellandrene or aromadendral. Some three species, however, appear to be of a distinctly higher type, namely, *E. salubris, E. occidentalis* and *E. marginata*. The oils of these species show a marked decrease in the amount of cineol they contain (with corresponding diminution of their solubility in alcohol) but contain the aldehyde aromadendral; phellandrene is still absent from these oils. Of the species described by Baker and Smith, only one (*E. gomphocephala*) is considered by these authors to have reached a high state of evolution. The evidence from which this conclusion is made, however, appears rather scant. The oil was obtained from the leaves in very poor yield (0.03 per cent.) and was largely a terpene oil; no details of the fractionation of

(1) R. T. Baker and H. G. Smith: A research on the Eucalypts, especially in regard to their essential oils. (Technical Education Series, No. 24, Technological Museum, N.S.W.)

(2) Phillips: Jour. Roy. Soc., W.A., Vol. IX., Part 2, 1923, p. 107.

the oil are given and the authors appear to base their classification on the fact that they were able to isolate phellandrene as its nitrosite (in unstated amount) from the oil. In addition, the leaf venation is not characteristic of the more highly evolved species, or is its fairly typical "Box" mark confined to such types.

Of the species examined by Phillips (*loc. cit.*) the oil of *E. campaspe* is of the predominant cineol-pinene type, but that of *E. spathulata* is unique. It contains a very high amount of cineol (two different specimens both showing about 65 per cent.) together with a normal amount of pinene, but in addition there is a considerable quantity, estimated as 2.5 per cent., of aromadendral present. Such a proportion of cineol in oils rich in aromadendral is unexpected. Baker and Smith's results, obtained from both Eastern and Western Australian species, indicate that oils which contain appreciable quantities of aromadendral rarely contain more than 30 per cent. of cineol (the usual amount being in the neighbourhood of 10 per cent.), or, as in the cases of *E. odorata* and *E. cneorifolia*, if the cineol is high (about 60 per cent.) then the aromadendral content is low. Baker and Smith give no figures for the estimation of the aldehydes in the majority of their oils, or their appropriate fractions, but an examination of their physical properties such as density, refractive index and optical rotation shows that the proportion is generally low, rarely exceeding 0.25 per cent. of the original oils.

None of the Western Australian oils so far examined shows any trace of the peppermint ketone, piperitone, which appears to be characteristic of the highest types of the eucalypts.

From the scant evidence at present available, it seems possible, then, that the majority of the Western Australian eucalypts occupy a fairly low position in the scale of evolution and it is the author's present intention to carry out a systematic examination of the Western Australian oils with a view, not only of increasing our knowledge concerning the distribution and composition of these oils, but in the hope of throwing more light on the question of the evolution of the eucalypts.

The present paper deals with the oil of *E. Flocktoniae* Maiden [3], known as "Merrit." The tree is described by Kessell and Gardner [4] and the material used was identified by Mr. C. A. Gardner, Government Botanist.

The oil for examination was obtained by steam distillation of leaves and terminal branches such as might be used in commercial practice. The material was collected during the last week in July by Mr. G. H. Burvill, B.Sc. (Hons.) from Fitzgerald Location 422, about 8 miles east of Circle Valley, near Salmon Gums.

The trees had been previously scorched by fire and the foliage was very dense and vigorous.

The leaves are lanceolate in shape, from ½in. to little more than ¾in. in width and from 3in. to occasionally 6in. in length. They are profusely dotted with oil glands which are visible as dark spots by reflected light and light spots by transmitted light. The venation is of the type exemplified by *E. globulus* and *E. Smithii* (Baker and Smith, *loc. cit.*), the marginal vein being somewhat removed from the edge and incurved at intervals to meet the lateral veinlets. The oil might therefore be expected to consist largely of cineol and pinene, and to contain no phellandrene.

(3) Maiden: Jour. Roy. Soc., N.S.W., Vol. 49, 1915, p. 316.
(4) Kessell and Gardner: A Key to the Eucalypts of Western Australia.

These expectations were realised, the oil being found to contain 46.2 per cent. of cineol and an estimated amount of about 10 per cent. of pinene. No evidence was found of phellandrene and aromadendral was absent. Nearly 75 per cent. of the oil distilled below 195°C., the rectified oil containing 61.5 per cent. of cineol. This is below the standard required (70 per cent.) by the British Pharmacopoeia for medicinal eucalyptus oils. The amount of free acids in the oil is very low and the saponification value indicates a low percentage of esters. The saponification value of the acetylated oil (the acetyl value) is, however, very high and indicates a high proportion of hydroxyl compounds. The sesquiterpene aromadendrene was shown to be present in some quantity. The oil is therefore of the predominant cineol-pinene type already discussed.

One interesting feature demands special mention. On fractional distillation of the oil, the formation of a white insoluble substance was noted just as the oil commenced to boil, the liquid becoming cloudy and opaque. This separation continued for some time, but as the distillation approached completion (in the neighbourhood of 200°C.), the precipitate commenced to redissolve, owing, doubtless, to its increased solubility in the residual material of high molecular weight, and to the higher temperature. The insoluble matter was isolated subsequently and it appeared to be identical in properties with the substance described by Baker and Smith (*loc. cit.*, p. 422) as being formed in certain eucalyptus oils on standing for some years, and that described by Phillips (*loc. cit.*, p. 109). Phillips makes no mention of the separation of this substance *during* the distillation of the oils studied by him, whilst Baker and Smith remark on its formation in only two instances. Both of these were oils of unknown botanical origin, one coming from Queensland and the other from Western Australia. The author has, however, observed this behaviour in all the oils so far examined (see Part II.) and has noted the formation of this insoluble body in the oil of *E. salmonophloia* which has stood for four months. It is hoped in the present series of investigations to isolate sufficient of this material to enable a more complete study of it to be made.

EXPERIMENTAL.

Distillation was carried out within eight days of collection, the leaves being green, unwrinkled and in good condition. The oil distilled rapidly, more than half coming over in the first hour; it was pale yellow in colour and had a fairly pleasant odour. The yield of undried oil was 1.75 per cent. by weight. After drying over anhydrous sodium sulphate, the crude oil had the following properties:—

Specific gravity at 20° C.	0.9216
Refractive index at 20° C.	1.4728
Optical rotation	+ 0.32°
Acid value	1.0
Saponification value	3.7
Acetyl value	96

The oil was soluble in 2 volumes of 70 per cent. (by weight) alcohol, indicating a low proportion of terpenes and other hydrocarbons.

The saponification value corresponds to 1.30 per cent. of esters calculated as geranyl acetate, $C_{12}H_{20}O_2$, whilst the acetyl value corresponds to 25.4 per cent. of alcohols calculated as geraniol, $C_{10}H_{18}O$. The cineol content,

determined by the method of the British Pharmacopoeia, using *o*-cresol, was 46.2 per cent. It did not restore the colour to Schiff's reagent and therefore contained no aldehydes. An alcoholic solution of the oil gave an intense yellow colour with neutral ferric chloride solution, suggesting the presence of phenolic bodies, and finally, it gave all the characteristic colour reactions of aromadendrene. Thus with bromine vapour, a solution of the oil in glacial acetic acid gave a crimson colour on the surface, which spread through the liquid, changing to violet and then indigo; with a drop of concentrated hydrochloric acid, a similar solution gave a deep crimson colour; on layering with concentrated sulphuric acid, a dark red colour was produced at the junction, which changed to a brownish-red on mixing, whilst with a syrupy solution of phosphoric acid, a brownish-yellow colour, changing to reddish, was formed at the boundary of the two liquids.

Fractionation.

120 grams of the oil were distilled under ordinary atmospheric pressure and the following fractions obtained:—

1.	Up to 150° C.	Nil
2.	From 150°-162° C.	8.5 per cent.
3.	From 162°-182° C.	57.2 „ „
4.	From 182°-195° C.	8.8 „ „
5.	From 195°-230° C.	8.65 „ „
	Residue	16.85 „ „

The separation of the insoluble white solid at the commencement of the distillation has already been discussed (page 103).

The rectified oil distilling below 195° C. (74.5 per cent.) contained 61.5 per cent. of cineol, corresponding to 45.8 per cent. in the original oil.

Fraction 2 was pale yellow in colour and had an odour resembling that of pinene. It had the following physical constants:—Specific gravity,* 0.8908; refractive index, 1.4623; optical rotation, + 25.67°. The fraction fairly obviously consisted largely of *d*-pinene, which was isolable in quantity in the form of its nitrosochloride (m.p. 104° C.).

Fraction 3, which made up the greater part of the distillate, was practically colourless and has a pleasant cineol-like odour. It had the following properties:—Specific gravity, 0.9078; refractive index, 1.4635; optical rotation, + 9.11°. The cineol content was approximately 64 per cent., but almost 85 per cent. of the oil was soluble in 50 per cent. resorcinol solution, indicating the presence of appreciable quantities of oxygenated compounds. The unabsorbed oil (15 per cent.) was taken up in ether, washed alternately with caustic soda solution and water, dried, the ether removed and the residue re-distilled. Somewhat more than half distilled below 164° C. (representing approximately 4.5 per cent. of the original oil); this consisted almost wholly of pinene, identified by its boiling point, odour and refractive index. A very small high boiling fraction was also obtained which slowly gave the reactions of aromadendrene.

Fraction 4 was colourless and gave slight reactions for aromadendrene. It had the following properties:—Specific gravity, 0.9392; refractive index, 1.4691; optical rotation, — 14.25°.

* Physical properties are given at 20° C. unless otherwise stated.

Fraction 5 was very pale yellow in colour and gave all the reactions described above for aromadendrene. It had the following properties:—Specific gravity, 0.9602; refractive index, 1.4888; optical rotation, — 29.60°. A high laevorotation in this fraction is generally considered to be indicative of the presence of aromadendral, cuminal or cryptal, but the fraction gave no reaction with Schiff's reagent, showing the absence of aldehydes.

The residue (16.85 per cent.) was taken up in ether, thus precipitating the white insoluble material discussed above. The precipitate was filtered off, washed with more ether, dried and weighed, 2.7 grams (corresponding to 2.25 per cent. of the original oil) being obtained. From the combined filtrates the ether was removed and the residue, which gave all the reactions for aromadendrene, was again fractionated under reduced pressure.

Two fractions were separated. The first distilled from 98° to 145° C. at 22 mms. pressure and made up 10 per cent. of the original oil. It was a clear yellow in colour and was fairly viscous; its optical rotation was — 15.27° and its refractive index 1.4989. The second fraction distilled from 145° to 165° C. at 22 mms. pressure and made up 3.2 per cent. of the original oil. It was a somewhat brownish-yellow in colour and was very viscous; its refractive index was 1.5044 but there was insufficient to measure its optical rotation. Both fractions were too viscous for their specific gravities to be determined by means of a pyknometer. The final residue consisted apparently of highly polymerised resinous materials which solidified to a dark reddish-brown mass on cooling.

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